CHAPTER VI

ESTIMATION

OF

ERRORS
Estimation of Errors

In this section we shall make an estimate of the errors in the calculated value of $g^E$. These errors are due to certain approximations or uncertainties in the experimentally measured quantities. The complete expression for the excess free energy of the mixture is given as,

$$g^E = x_1RT(\ln \frac{P_{y_1}}{P_{y_1}x_1}) + (V_1-B_{11})(P-P_1) + P\delta_{12}y_2^2$$

$$+ x_2RT(\ln \frac{P_{y_2}}{P_{y_2}x_2}) + (V_2-B_{22})(P-P_2) + P\delta_{12}y_1^2$$

$$+ (P^*-P)\gamma^E$$

..... (6.1)

This expression is derived on the basis that imperfect behaviour of the vapour phase can be taken care of by second virial coefficient. The last term in this equation is the correction for bringing all the mixtures to a common pressure $P^*$ (for convenience $P^*$ may be taken equal to one atmosphere) is quite negligible and in no case is greater than 0.05 Joules.

The second approximation made here is that $\delta_{12}$ is zero, that is the virial coefficient $B_{12} = (1/2) (B_{11} + B_{22})$. This may lead to uncertainty of the order of 20 in the value of $B_{12}$ which in turn makes a contribution of 0.1 Joule/mole in $g^E$ and hence this term may also be neglected.

Neglecting these two terms from equation (6.1) we get,
Replacing in the above equation \( P_{y1} = P_1 \) and \( P_{y2} = P_2 \) that is the partial pressures of the components in the gas phase, we write the equation,

\[
g^E = x_1 RT(\ln \frac{P_{y1}}{P_1 x_1}) + (V_1 - B_{11})(P - P_1) + x_2 RT(\ln \frac{P_{y2}}{P_2 x_2}) + (V_2 - B_{22})(P - P_2) \quad \ldots \quad (6.2)
\]

There is no direct measurement of the uncertainties in the values of \( P_1 \) and \( P_2 \). To evaluate uncertainties in individual partial pressures it is assumed that the following relations are valid,

\[
dP_1' = \left(\frac{P_1}{P_1 + P_2}\right) \sigma \quad ; \quad dP_2' = \left(\frac{P_2}{P_2 + P_1}\right) \sigma \quad \ldots \quad (6.4)
\]

where,

\[
\sigma = \sqrt{\sum R^2 / (n - n_g)} \quad \ldots \quad (6.5)
\]

where, \( n \) is the number of points and \( n_g \) is the number of arbitrary constants in equation (5.1). Variations of \( g^E \) with each of the experimental quantities are given by the following expressions,

\[
\frac{\delta g^E}{\delta P_1'} = x_1 RT \left(\frac{1}{P_1'}\right) = A \quad \ldots \quad (6.6)
\]
\[ \frac{\partial g^E}{\partial P} = x_1 (B_{11} - V_1) + x_2 (B_{22} - V_2) \]
\[ \frac{\partial g^E}{\partial P_1} = -x_1 \left( \frac{RT}{P_1} + (B_{11} - V_1) \right) \]
\[ \frac{\partial g^E}{\partial P_2} = -x_2 \left( \frac{RT}{P_2} + (B_{22} - V_2) \right) \]
\[ \frac{\partial g^E}{\partial x} = 2RT \ln \frac{P_1}{P_2} \left( \ln P_1 / P_2 - \ln P_1 / P_2 \right) \]
\[ + (P - P_1) (B_{11} - V_1) - (P - P_2) (B_{22} - V_2) \]
\[ \text{And the variation of } g^E \text{ due to the variation of quantities} \]
\[ \text{(pressures and partial pressures) caused by the drift in the temperature (± 0.01°C) can be written as}, \]
\[ F = (\Delta \frac{\partial P_1}{\partial T} + B(\frac{\partial P_2}{\partial T}) + C(\frac{\partial P}{\partial T}) + D(\frac{\partial P_1}{\partial T}) + E(\frac{\partial P_2}{\partial T})) \]
\[ \text{Neglecting the contribution due to uncertainty in composition which is very small (equation 6.11), total uncertainty in the value of } g^E \text{ is given by}, \]
\[ g^E = \sqrt{(A dP_1)^2 + (B dP_2)^2 + (C dP)^2 + (D dP_1)^2 + (E dP_2)^2 + (F dT)^2} \]
\[ \text{In case of mixtures having one component non-volatile the uncertainty is only from the contribution of the volatile component.} \]
\[ Y_1 = \left( \frac{P}{P_1 x_1} \right) \exp \left( (P - P_1)(B_{11} - V_1) / RT \right) - B_{11} 2 p^2 (p - P_1^2) / 2 R T^2 \]
The uncertainty in \( \dot{g}^E \) arises from the uncertainty due to \( \gamma_1 \)
and \( \gamma_2 \), which arises from the measurable quantities, total
pressure and pressure of the pure component.

\[
\frac{\partial \ln \gamma_1}{\partial P} = \frac{1}{P} + \frac{(B_{11} - V_1)/RT}{P} - B_{11}^2 \frac{P}{RT^2}
= A \quad \ldots (6.15)
\]

and,

\[
\frac{\partial \ln \gamma_1}{\partial P} = \frac{1}{P_1} - \frac{(B_{11} - V_1)/RT}{P_1} + B_{11}^2 \frac{P}{RT^2} \frac{T^2}{T_2}
= B \quad \ldots (6.16)
\]

The final form for uncertainty in \( \ln \gamma_1 \) is then given by,

\[
\Delta (\ln \gamma_1) = \sqrt{(AdP)^2 + (BdP)^2} \quad \ldots (6.17)
\]

The uncertainty due to errors in composition and
temperature are negligible and have not been taken into account.

Then,

\[
\Delta g^E = RT \chi_1 \Delta \ln \gamma_1 + RT \chi_2 \Delta \ln \gamma_2 \quad \ldots (6.18)
\]

\[
= RT \Delta \ln \gamma_1 \quad \ldots (6.19)
\]

From the uncertainty in \( g^E \) at different temperatures one
can also estimate the uncertainty in \( h^E \), by using Gibbs-Helmholtz
equation,

\[
(\partial g^E_2 / T_2) - (\partial g^E_1 / T_1) = \Delta h^E (1/T_1 - 1/T_2) \quad \ldots (6.20)
\]
where, \( \Delta h^E \) is the uncertainty in excess enthalpy. These uncertainties in \( g^E \) and \( h^E \) values have been calculated and are given at the appropriate places in the next chapter.